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Bioinspired Surface Treatments for Improved Decontamination: Improved POSS Treatments

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14. ABSTRACT
This effort evaluates bioinspired coatings for use in a top-coat type application to identify those technologies that may improve decontamination capabilities for painted surfaces. This report details results for evaluation of polyhedral oligomeric silsesquioxane (POSS) surface treatments. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphate, and diisopropyl fluorophosphates following treatment of contaminated surfaces with a soapy water solution is reported. Wetting behaviors and target droplet diffusion on the surfaces are also discussed.

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EXECUTIVE SUMMARY

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) initiated a program in January 2015 for evaluation of bioinspired treatments suitable for use as a top coat on painted surfaces with the intention of achieving improved aqueous decontamination of these materials. Funding was provided by the Defense Threat Reduction Agency (DTRA, CB10125). This report details results for evaluation of polyhedral oligomeric silsesquioxane (POSS) surface treatments. POSS are cage structures of silicon and oxygen that bind to organic polymers producing chains that can serve to reinforce the overall structure. A previous report (NRL/MR/6930--18-9775) addressed an initial set of POSS treatments. That effort allowed identification of promising approaches for improving performance in the POSS topcoats. The POSS variants evaluated under the current study included a three cage structures with iso-octyl side chains (AM0270, MA0719, and TH1555) and an open cage structure with trifluoropropyl side chains (SO1465). The materials were deposited on polyurethane paint coated aluminum coupons. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, and diisopropyl fluorophosphate following treatment of contaminated surfaces with a soapy water solution is reported along with droplet diffusion on the surfaces and wetting angles.

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BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: IMPROVED POSS TREATMENTS

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide technologies for protection of forces in a contaminated environment, including those for contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort funded through the Defense Threat Reduction Agency (DTRA, CB10125) intended to evaluate and develop top-coat type treatments suitable for application to painted surfaces that would reduce retention of chemical threat agents following standard decontamination approaches. The effort sought to survey relevant and related areas of research and evaluate identified technologies under appropriate methods to determine efficacy, scalability, and durability. The current document summarizes results for one of the identified technologies. In this case, a series of polyhedral oligomeric silsesquioxane (POSS) prepared by Hybrid Plastics Inc. This series of materials was selected based on lessons learned from a set of evaluations. That work was summarized in NRL/MR/6930--18-9775.[1]

POSS treatments were initially evaluated as an alternative for achieving the behaviors noted for slippery liquid-infused porous surfaces (SLIPS)[2-9] or slippery omniphobic covalently attached liquids (SOCAL),[10, 11] while avoiding the durability issues noted for those materials. Polyhedral oligomeric silsesquioxanes (POSS) are cage structures of silicon and oxygen that bind to organic polymers providing molecular level reinforcement. They are used to enhance the mechanical properties of polymers (scratch resistance or increased modulus, for example) and thermal stability. They can also be used as flow aids, dispersants, lubricants, and surface modifiers. The POSS variants of the initial study[1] included a cage structure with methacrylate side chain (MA0702), two variants using a cage structure with methoxylated polyethylene glycol side chain (PG1192 and PG1193), two variants using the Corin XLS polyimide structure (Corin XLS and Corin 0578) and two cage structures with alkyl groups of varied length (SO1450 and SO1455; Figure 1).

The initial POSS treatments provided interesting results with wetting and target retention behaviors varying widely across the coating types. Different coatings provided better resistance to retention of individual targets, but no material provided dramatically improved overall performance. Highlights of those results indicated the potential of the FL0578 as a mobile lubricant as well as generally better performance in the PG1193 and SO1455 coatings. The current study utilizes materials identified based on those promising results, including three materials with isooctyl side chains (AM0270, MA0719, and TH1555) as well as a fluorinated structure (Figure 2).

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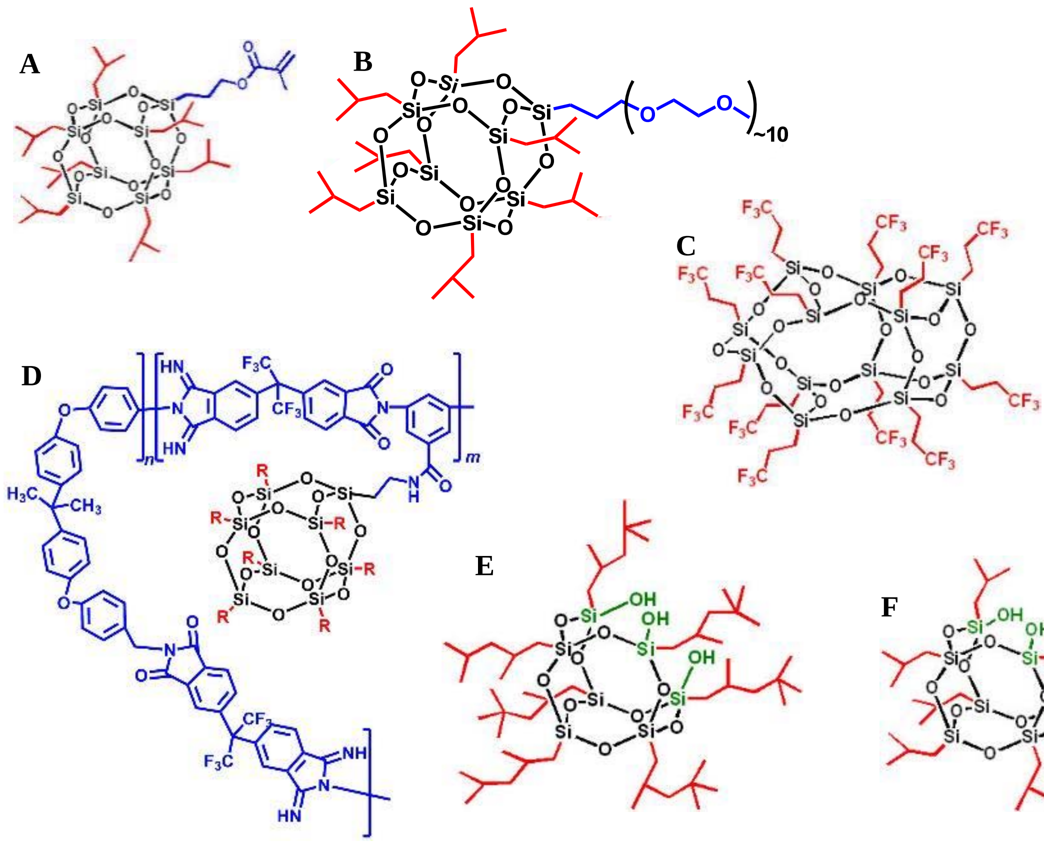

Fig. 1 — Molecular structures for the initial POSS variants: methacryloisobutyl POSS (A; MA0702); methoxyPEGisobutyl POSS (B; PG1192); trifluoropropyl POSS (C; FL0578); Corin XLS Polyimide (D); trisilanolisoocytl POSS (E; SO1455); and trisilanolisobutyl POSS (F; SO1450).[1]

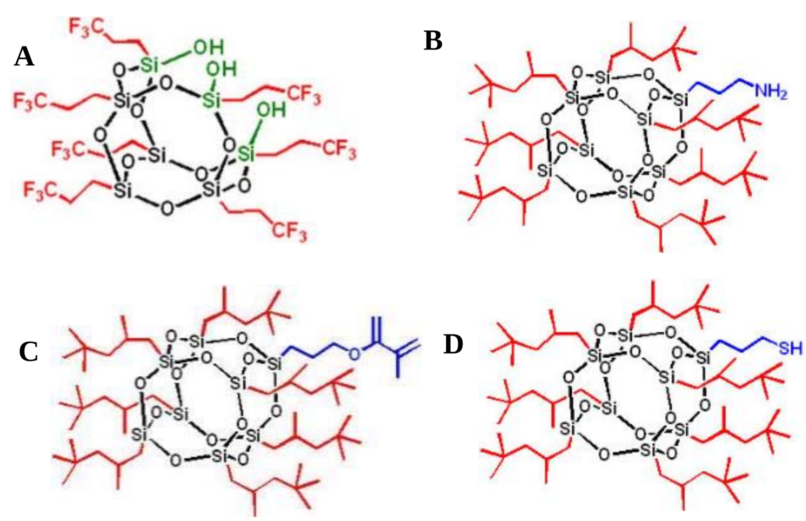

Fig. 2 — Molecular structures for the new POSS variants: hepta-trifluoropropyl trisilanol POSS (A; SO1465) aminopropylisooctyl POSS (B; AM0270); methacrylisooctyl POSS (C; MA0719); and mercaptopropylisooctyl POSS (D; TH1555).

AM0270 is comprised of the POSS cage structure with isooctyl groups at the corners and an aminopropyl group. It is used as a grafting agent and can be applied to increase hydrophobicity. MA0719 is similar to the previously evaluated MA0702. This POSS cage structure is also modified with isooctyl groups at the corners and bears a methacrylate group. MA0719 is a commoner used for increasing hydrophobicity and toughness. Like MA0719 and AM0270, TH1555 is POSS cage structure modified with isooctyl groups at the corners. This structure bears a mercaptopropyl group and is used for surface modification, plasticization, and increasing hydrophobicity. SO1465 was included here based on the performance of the Corin formulation modified with trifluoropropyl POSS (FL0578; Figure 1). SO1465 provides a similar fluorinated structure on the open cage base of SO1450 and SO1455. Fluorinated POSS are used for reducing surface energy, while the open corner leaves three active silanol groups for attachment to the polyurethane paint surface. (Figure 2).

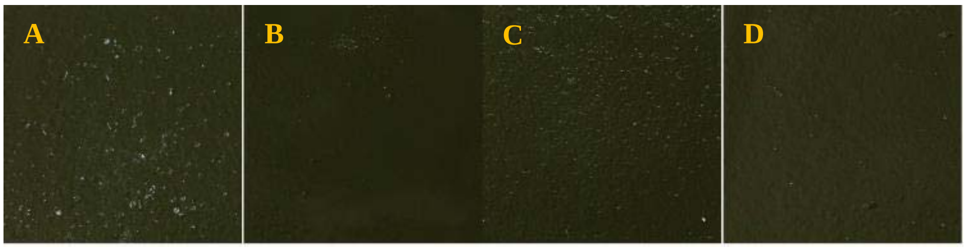

Fig. 3 — Images of painted coupons with hepta-trifluoropropyl trisilanol POSS (A; SO1465) aminopropylisooctyl POSS (B; AM0270); methacrylisooctyl POSS (C; MA0719); and mercaptopropylisoctyl POSS (D; TH1555).

For the complete system evaluated under this study, aluminum coupons were coated with a polyurethane paint system by NRL and were provided to Hybrid Plastics Inc (Figure 3). Following deposition of the POSS variants, coupons were returned to NRL for evaluation using standard approaches including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds.

METHODS

Sessile contact angles for samples evaluated under this effort used three 3 μL droplets per surface with each droplet measured independently three times for each of three targets, water, ethylene glycol, and *n*-heptane. Geometric surface energy was calculated based on the water and ethylene glycol interactions using software designed for the DROPimage goniometer package. Sliding angles were determined using 5 μL droplets. The droplet was applied at 0° after which the supporting platform angle was gradually increased up to 60°. Sliding angles for each of the liquids were identified as the angle for which movement of the droplet was identified. Shedding angles for each liquid were determined using 12 μL droplets initiated 2.5 cm above the coupon surface. Changes in base angle of 10° were utilized to identify the range of droplet shedding angle based on a complete lack of droplet retention by the surface (not sliding). The angle was then reduced in steps of 1° to identify the minimum required angle. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. Droplets of 5 μL were applied to the surfaces and images were collected at 30 s intervals for 5 min followed by images at 5 min intervals for a total of 30 min. DFP samples were kept covered for the duration of the experiment to minimize evaporation. In some cases, reflections from the glass cover can be seen in the images.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM).[12] Standard target exposures utilized a challenge level of 10 g/m^2. The painted coupons were 0.00101 m^2; the 10 g/m^2 target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water (0.59 g/L Alconox in deionized water). The rinsed coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For paraoxon, methyl salicylate (MES), diisopropyl fluorophosphate (DFP), and dimethyl methylphosphonate (DMMP) analysis, gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex Rtx-5 (30 m x 0.25 mm ID x 0.25 μm df) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of 200°C was used with a 1:1 split ratio at a flow rate of 3.6 mL/min at 69.4 kPa. The oven gradient ramped from 50°C (1 min hold time) to 180°C at 15°C/min and then to 300°C at 20°C/min where it was held for 5 min.

RESULTS

Analysis of the support surface in the absence of additional coatings provides a point of comparison for evaluating the benefits of the surface treatments. Each table includes data on the relevant support material, a painted aluminum coupon, and for a Fomblin Y lubricated painted aluminum coupon. Results for PG1193 and SO1455, materials considered under the initial POSS evaluation, are also included for comparison. Application of the POSS coatings considered here reduced the surface energy of the painted surface (Table 1 and Figure 4). The hepta-trifluoropropyl trisilanol POSS structure (SO1465) yielded the lowest surface energy with wetting behaviors similar to those of the MA0702 of the original study. The isooctyl modified POSS show behaviors similar to that of the initially evaluated SO1455, which also included isooctyl side chains. All of the POSS surfaces were fully wetted by heptane. No sliding or shedding from the surfaces was noted below an incline of 60°.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 6; Appendices). For these studies, droplets of the simulants (5 μL) were utilized. The spread of the droplets was quantified by measuring the diameter of the droplets in the images over time (Figure 7). For the paint only samples, MES and DFP spread quickly, reaching the edges of the coupon at 10 and 2 min, respectively. DMMP does not spread during the course of the 30 min incubation. The POSS materials produced a range of results. DMMP behavior was unchanged following application of the POSS coatings; application of Fomblin Y had a negative impact on permeation of this target. MA0719 and TH1555 significantly reduced the spread of MES across the surface while AM0270 resulted in MES behavior similar to that of the Fomblin Y oiled surface. All of the POSS treatments reduced the spread of DFP, with AM0270 yielding the largest effect. In the prior POSS study, spread of the three simulants was nearly completely prevented by the Corin XLS and Corin 0578 coatings.

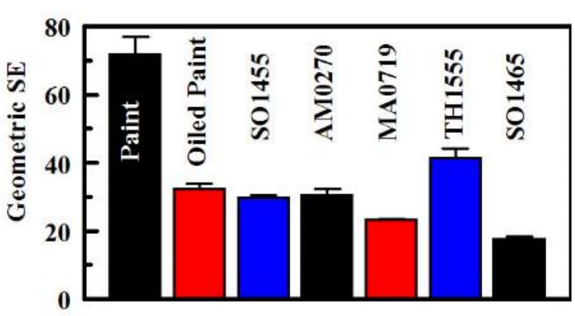

Fig. 4 — Geometric surface energy (mJ/m^2) for the evaluated coatings. PG1193 was fully wetted by water and heptane preventing calculation of values for these surfaces.

Table 1 – Sessile, Sliding, and Shedding Contact Angles on Aluminum Supports

Coupon	**Liquid**	**Sessile Angle**	**Sliding Angle**	**Shedding Angle**	**Geometric Surface Energy (mJ/m^2)**
Aluminum Support					
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	--	--	
Fomblin Y Oiled Paint	water	73.1 ± 2.1	>60	46.7 ± 3.3	32.2 ± 1.6
	ethylene glycol	52.5 ± 0.61	>60	49.8 ± 4.9	
	n-heptane	40.1 ± 2.9	>60	36.6 ± 3.3	
PG1193	water	--	--	--	--
	ethylene glycol	8.7 ± 0.2	--	--	
	n-heptane	--	--	--	
SO1455	water	73.8 ± 1.1	>60	>60	29.8 ± 0.7
	ethylene glycol	58.6 ± 0.3	>60	>60	
	n-heptane	--	--	--	
New POSS Treatments					
AM0270	water	77.7 ± 1.5	>60	>60	30.4 ± 1.9
	ethylene glycol	56.7 ± 2.0	>60	>60	
	n-heptane	--	--	--	
MA0719	water	86.5 ± 0.4	>60	>60	23.2 ± 0.3
	ethylene glycol	67.1 ± 0.7	>60	>60	
	n-heptane	--	--	--	
TH1555	water	84.7 ± 0.7	>60	>60	41.4 ± 2.9
	ethylene glycol	48.9 ± 1.9	>60	>60	
	n-heptane	--	--	--	
SO1465	water	92.2 ± 1.2	>60	>60	17.6 ± 0.7
	ethylene glycol	78.2 ± 1.4	>60	>60	
	n-heptane	--	--	--	

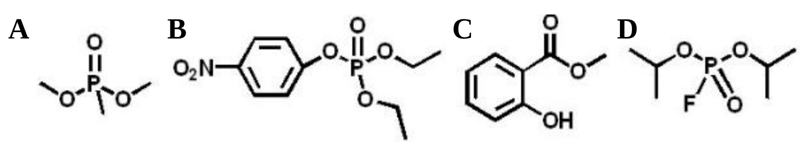

Fig. 5 — Structures of simulants used under this study: dimethyl methylphosphonate (DMMP; A), paraoxon (B), methyl salicylate (MES; C), diisopropyl fluorophosphates (DFP; D).

The coupons were subjected to several cycles of simulant exposure (10 g/m^2), aging, washing, and drying over a period of several weeks (Figure 5). With the exception of the SO1465, little change in the appearance or wetting characteristics was observed over these processing steps. Similarly to the POSS materials of the previous study, marking and damage to the SO1465 coating was noted, especially following the DFP challenge. When the soapy water process was employed (Figure 8; Table 2), retention of all targets was less for the Fomblin Y lubricated paint treatments than for the paint only surfaces. The MA0702 coating reduced retention of DFP and paraoxon but increased retention of MES and DMMP as compared to the oiled surface. The SO1465 reduced retention of all targets except DFP for which retention was significantly increased. AM0270 and TH1555 reduced retention of paraoxon, MES, and DMMP and had little impact on DFP retention. These results represent a distinct improvement over the POSS treatments of the original study and over those noted for the Fomblin Y lubricated surface. Overall, the TH1555, with isooctyl groups and a mercaptopropyl group, offered the lowest retention of targets.

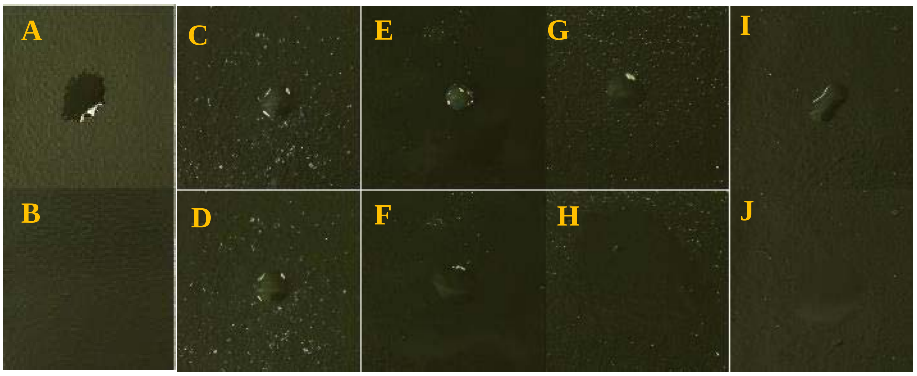

Fig. 6 — Images of coupons at 0 and 30 min following MES exposure: painted coupon (A & B) and painted coupon with SO1465 (C &D), AM0270 (E & F), MA0719 (G & H), and TH1555 (I & J).

For comparison, paint only coupons retained significant amounts of target at 5.48, 6.20, 4.28, and 0.52 g/m^2. When no rinsing or decontamination steps were used, paint only coupons retained the following: paraoxon – 9.84 g/m^2, MES – 9.54 g/m^2, DMMP – 9.90 g/m^2, DFP - 7.39 g/m^2. Though the nominal target application was 10 g/m^2, recovery from surfaces was always less than this value. Losses due to evaporation would be expected, especially for DFP. Additional losses likely occur during rinse steps due to agent interaction with the untreated region of the coupon; the back of these coupons is unpainted aluminum.

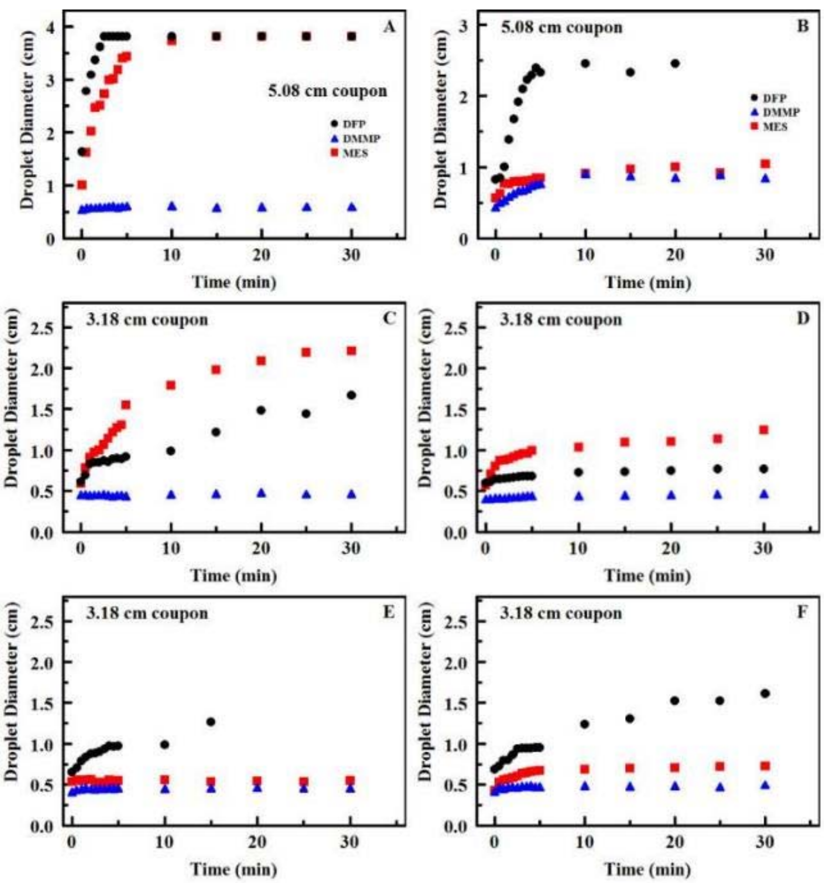

Fig. 7 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a painted coupon (A) and painted coupons lubricated with Fomblin Y (B) or treated with hepta-trifluoropropyl trisilanol POSS (C; SO1465); aminopropylisooctyl POSS (D; AM0270); methacrylisooctyl POSS (E; MA0719); and mercaptopropylisooctyl POSS (F; TH1555).

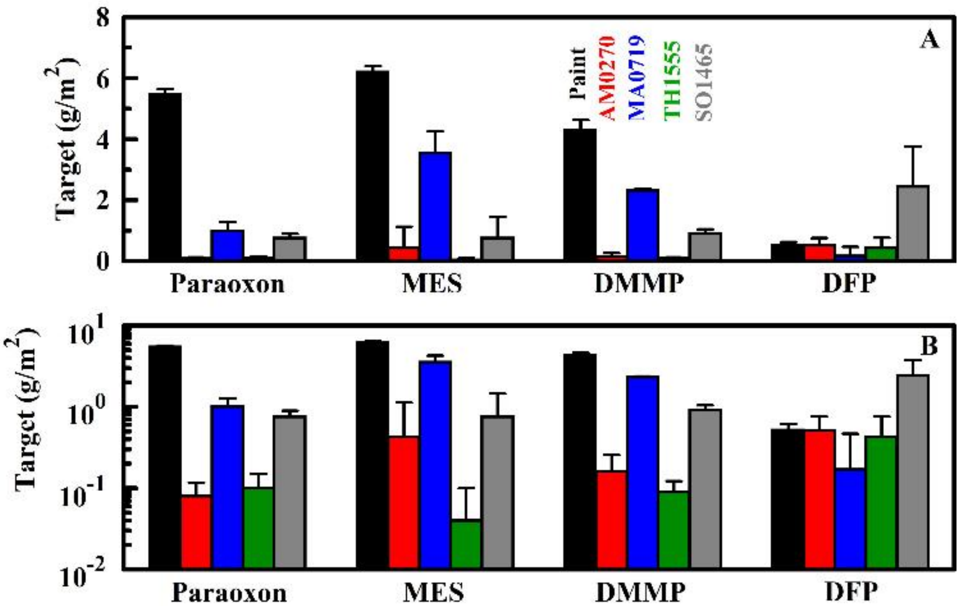

Fig. 8 — Target retention by coupons following treatment with an air stream and rinsing with soapy water shown on a linear scale (A) and (B) on a log scale: painted (black), AM0270 (red), MA0719 (blue), TH1555 (green), and SO1465 (gray).

Table 2 – Target Retention (g/m^2) Following 1 h Aging on Aluminum Supports

Coupon	Paraoxon	MES	DMMP	DFP
Aluminum Support				
Paint Only	5.48	6.20	4.28	0.52
Fomblin Y Oiled Paint	1.24	2.85	0.59	0.34
AM0270	0.08	0.43	0.16	0.51
MA0719	1.00	1.61	2.31	0.17
TH1555	0.10	0.04	0.09	0.43
SO1465	0.75	0.75	0.91	2.44
Original POSS Materials Considered				
MA0702	1.22	5.45	0.46	1.52
PG1192	2.58	1.98	ND	0.68
PG1193	2.14	1.41	ND	0.22
Corin XLS	3.23	6.46	0.22	3.74
Corin 0578	1.76	8.87	0.16	4.55
SO1455	1.67	4.33	ND	0.48
SO1450	3.40	6.82	ND	1.70

ND = not detected

CONCLUSIONS

The POSS samples of the original study[1] yielded interesting results with wetting and target retention behaviors varying widely across the POSS structures. Different coatings provided better resistance to retention of individual targets, but did not provide overall improved performance. The materials considered here provided significantly improved performance over both the painted surface and the materials of the original study. These materials offer interesting potential for improved paint performance as the process for application of the materials can be simple. Additional improvements in performance may be obtained through combining a structure similar to the SO1465 of this study or the SO1455 of the original study with an alkane or fluoroalkyl group at the open corner position. The MS0805 structure currently available in the Hybrid Plastics catalog offers another possibility for further improving performance in these coatings (Figure 9). In addition to enhanced performance, this second series of POSS samples addressed the damage noted on repeated use of the original materials. Here, the isooctyl materials did not show evidence of damage during processing. Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. It may also be of interest to consider the impact of aging on these materials.

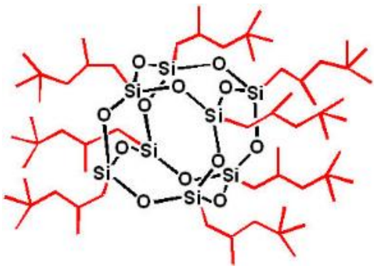

Fig. 8 — Molecular structures for an additional POSS variant, isooctyl POSS (MS0805).

ACKNOWLEDGEMENTS

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Appendix A

AM0270 COUPON IMAGES

Fig. A1 — DFP on AM0270. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

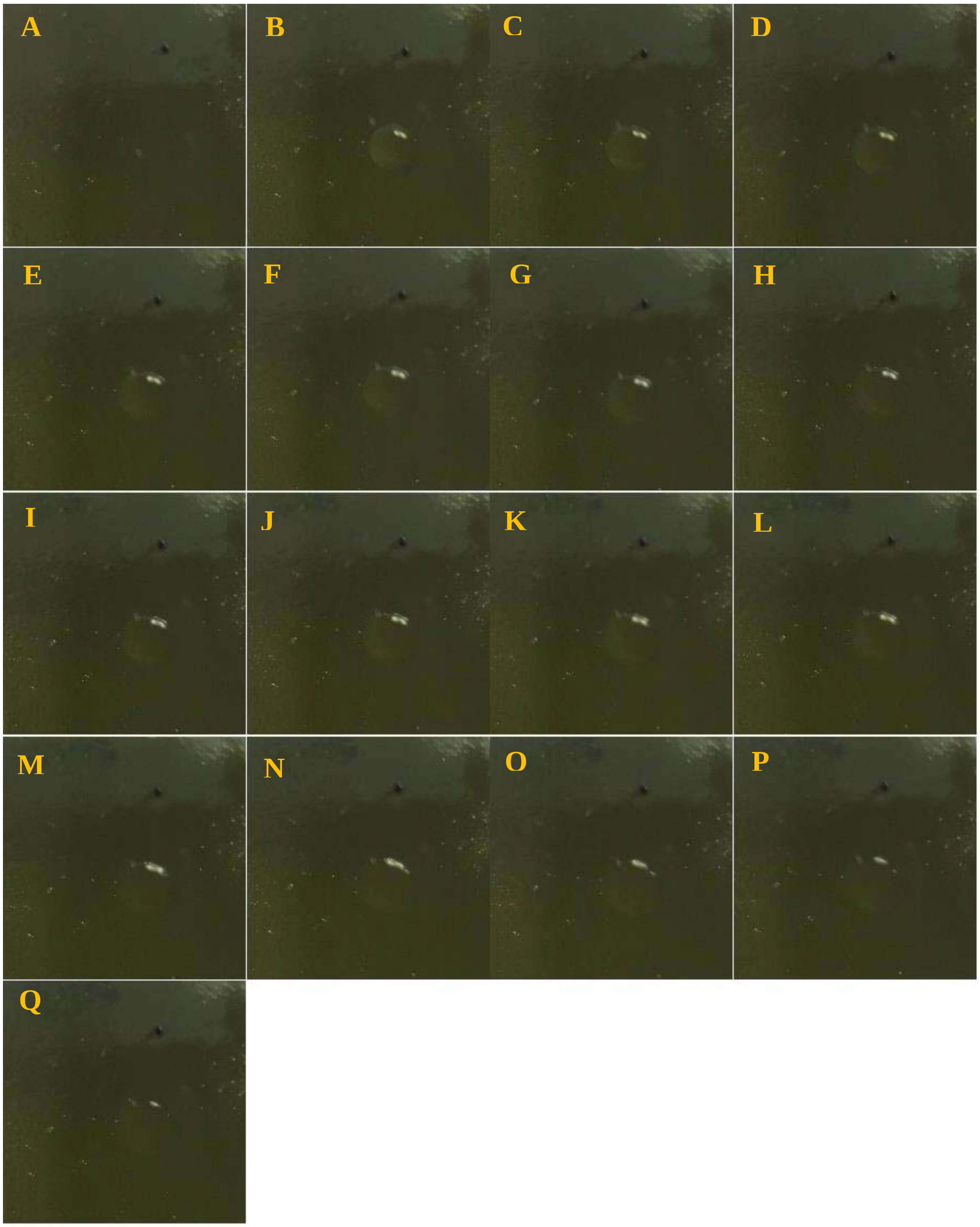


Fig. A2 — MES on AM0270. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

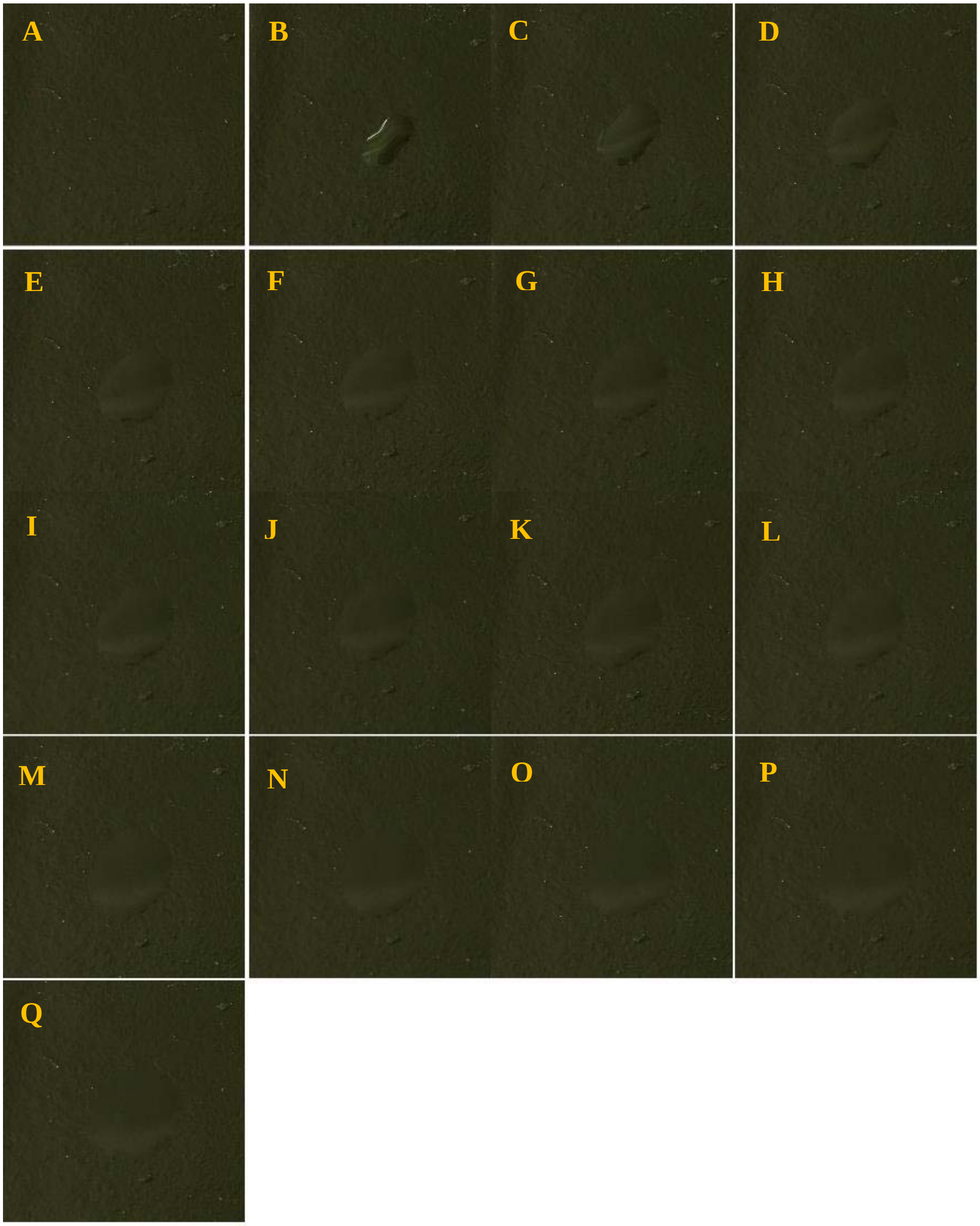
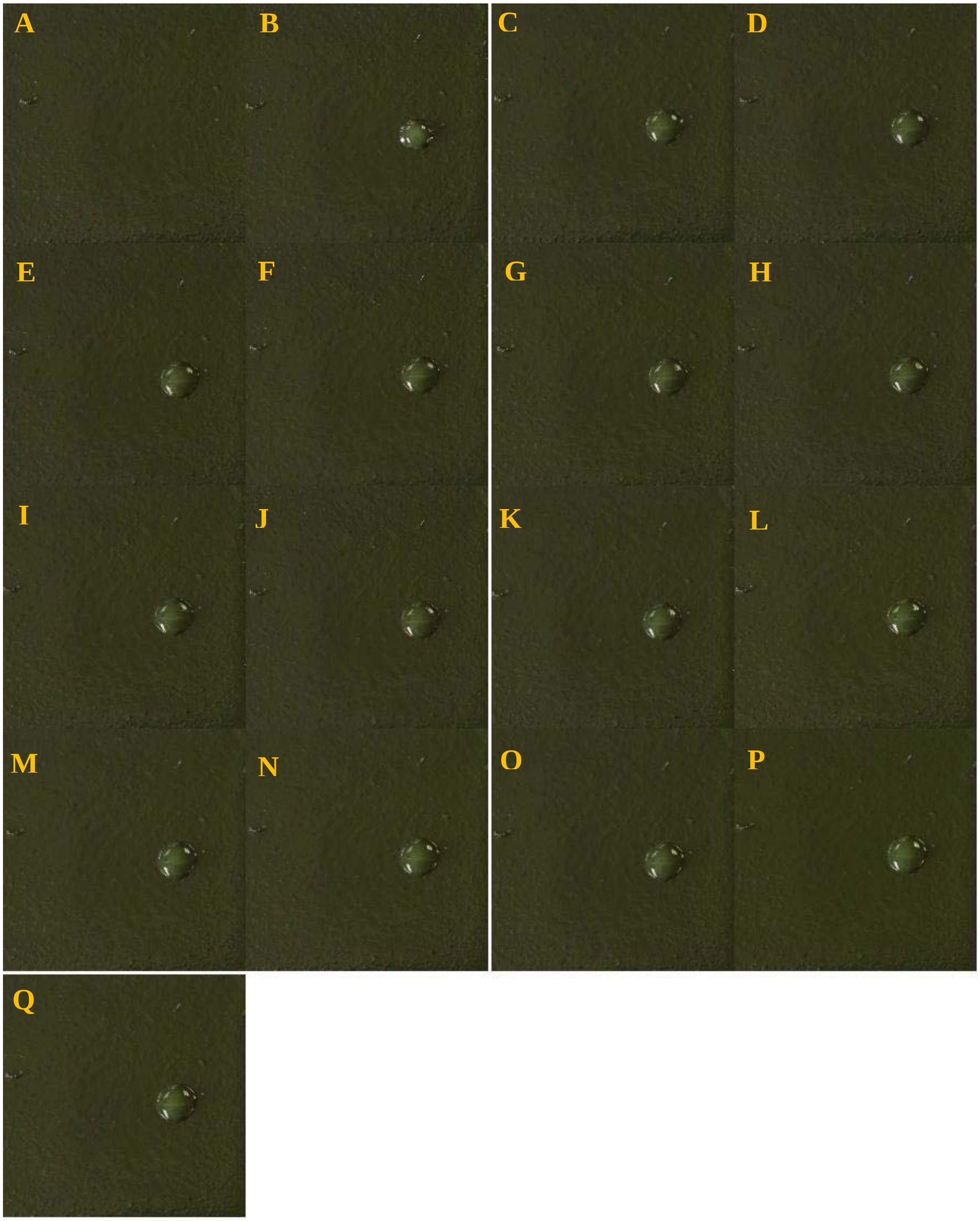


Fig. A3 — DMMP on AM0270. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

MA0719 COUPON IMAGES

Fig. B1 — DFP on MA0719. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

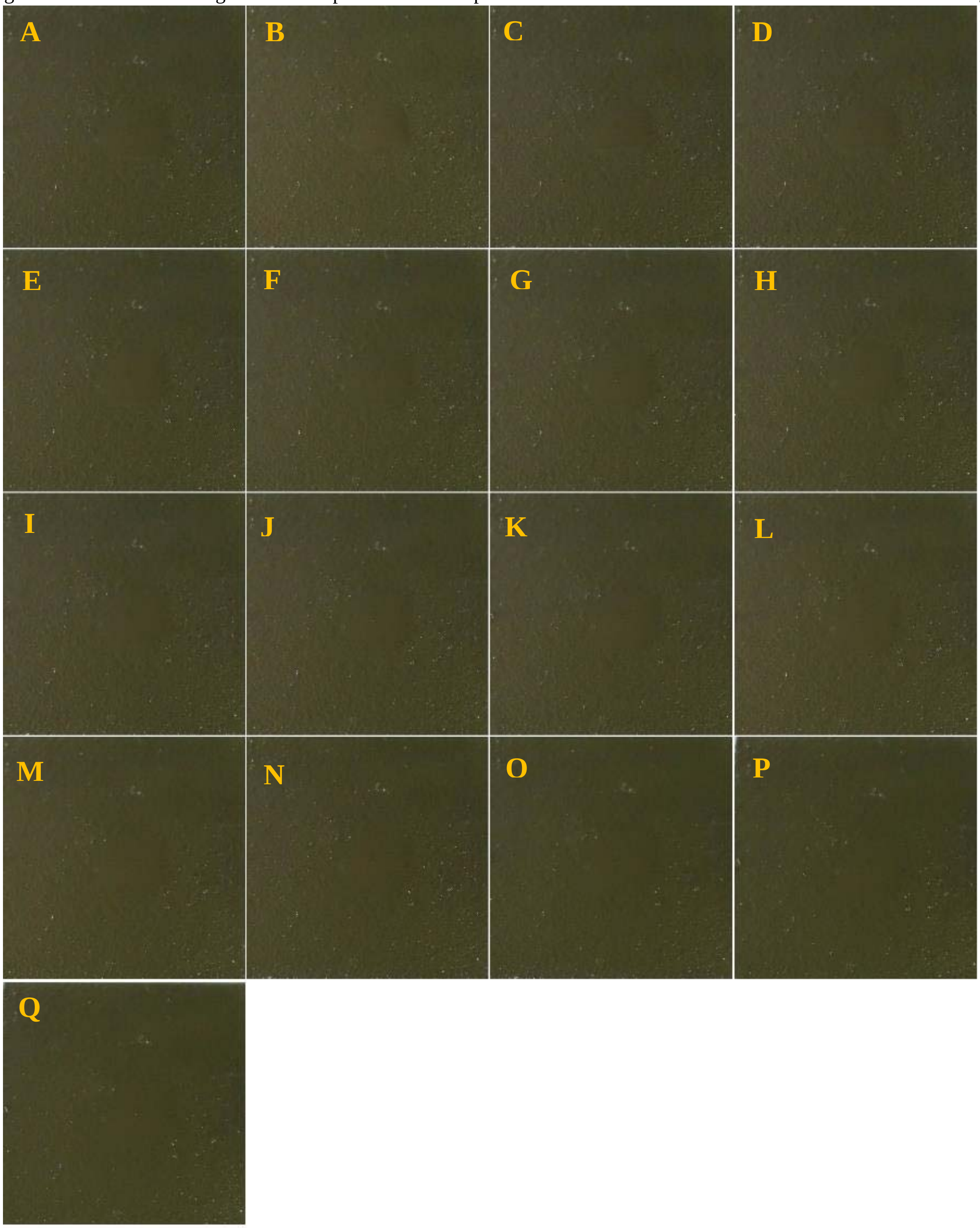


Fig. B2 — MES on MA0719. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

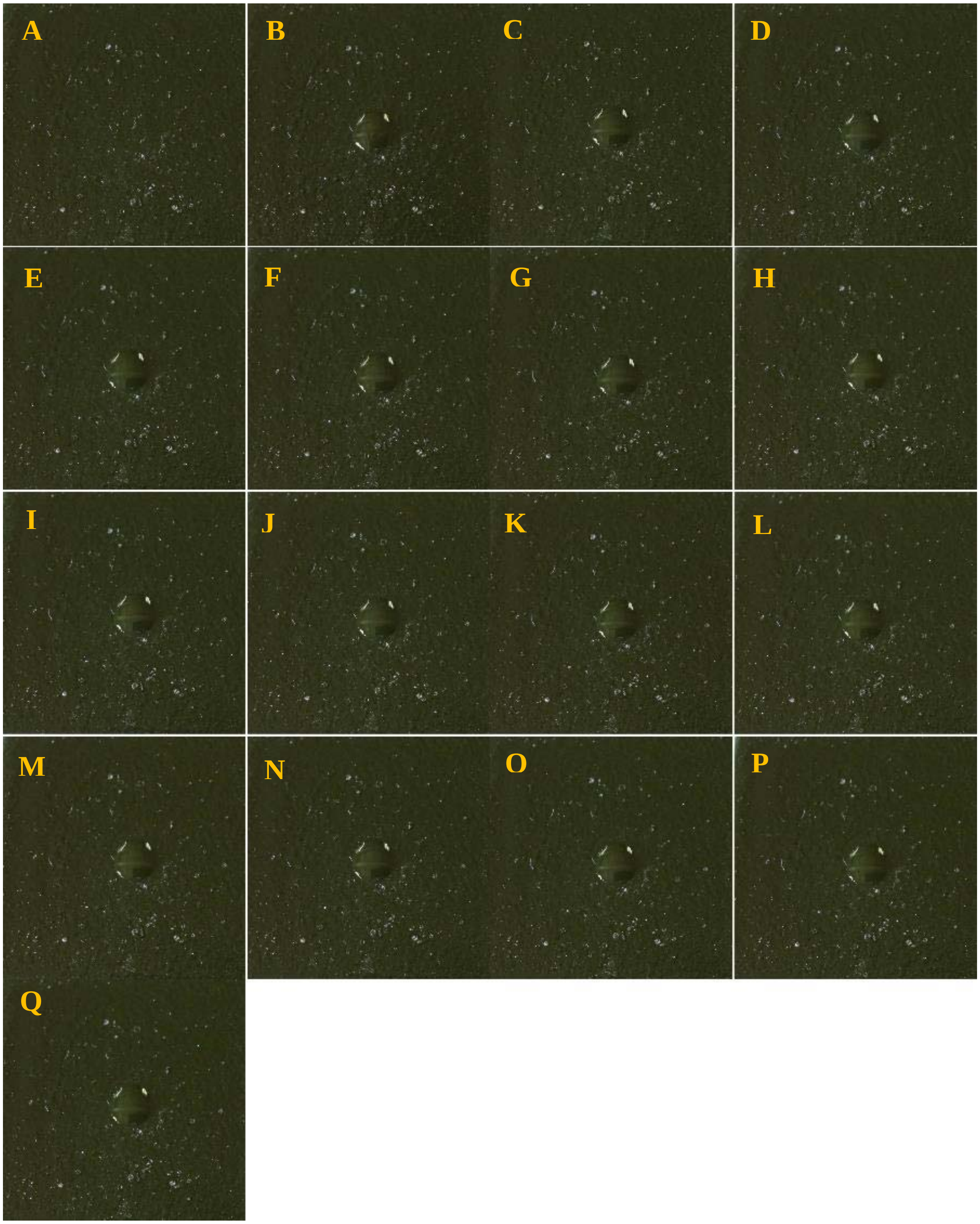
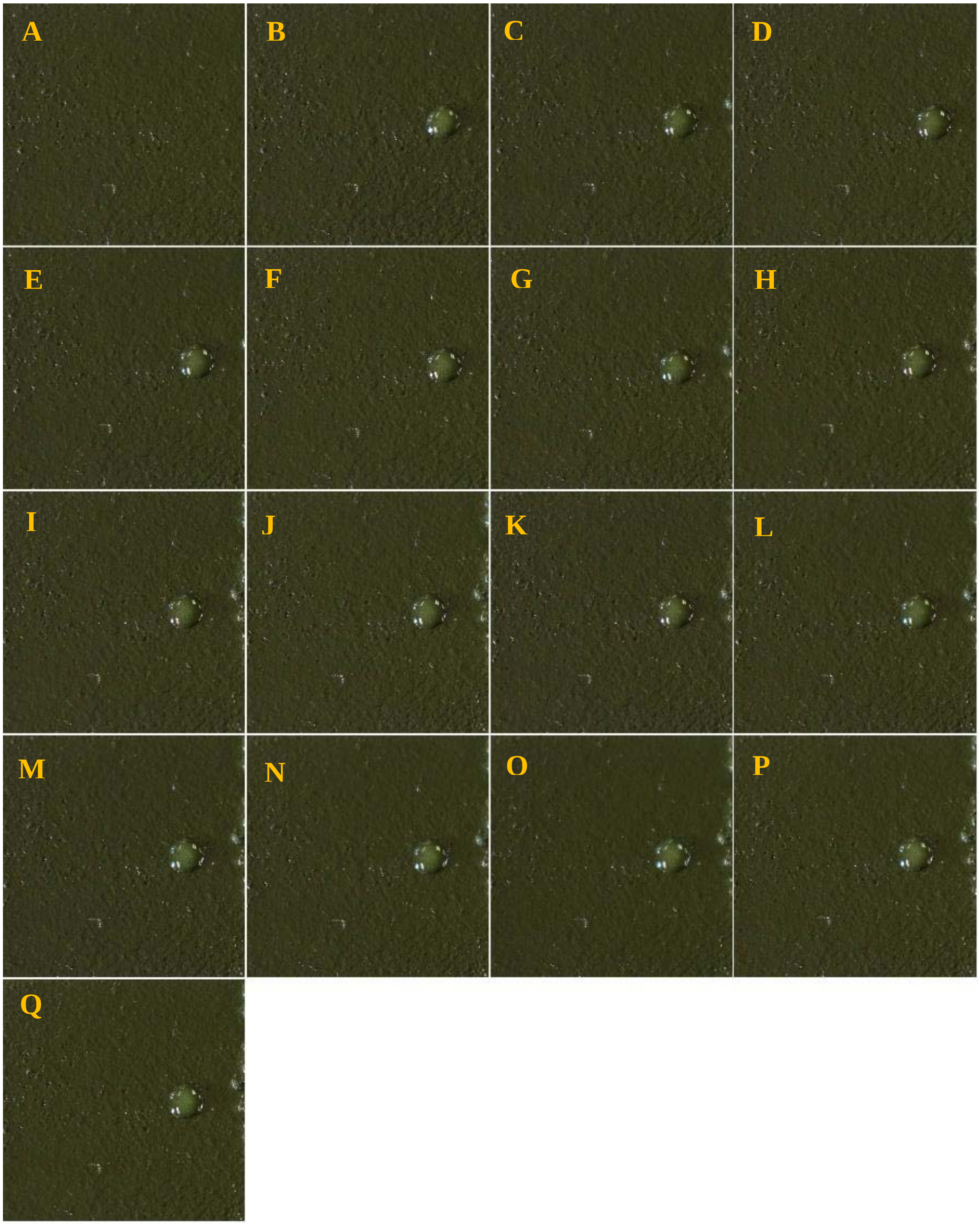


Fig. B3 — DMMP on MA0719. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix C

TH1555 COUPON IMAGES

Fig. C1 — DFP on TH1555. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

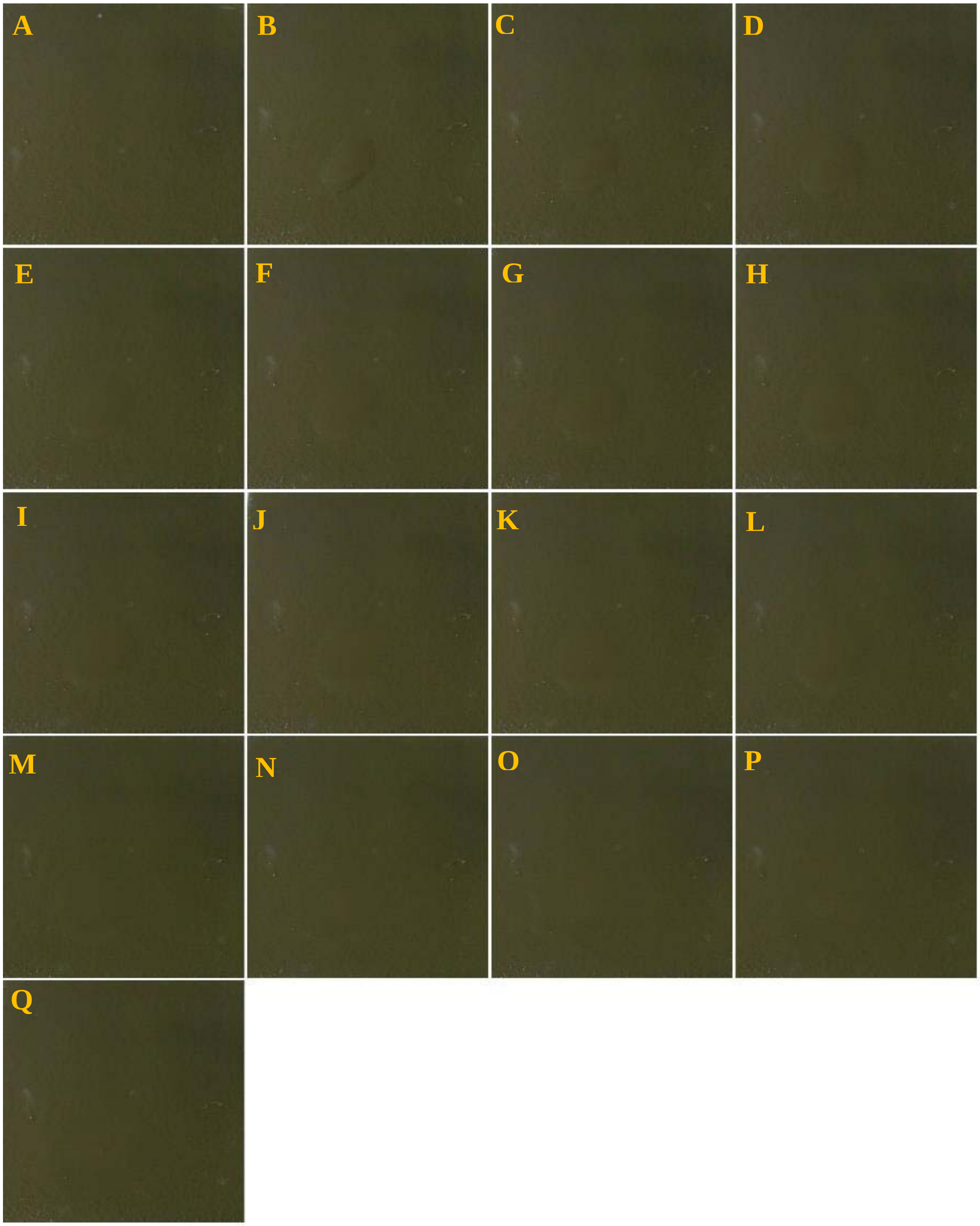


Fig. C2 — MES on TH1555. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

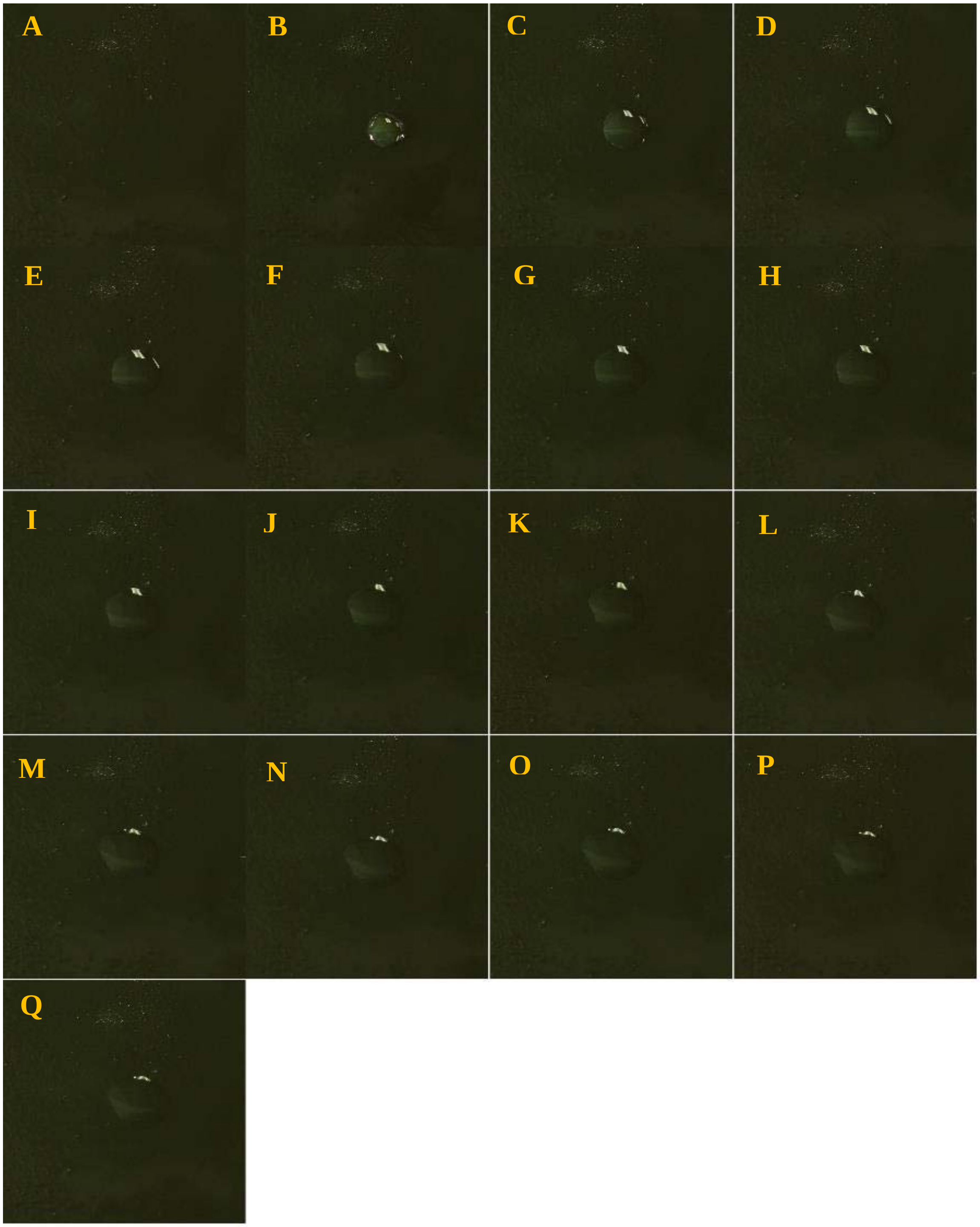


Fig. C3 — DMMP on TH1555. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

Appendix D

SO1465 COUPON IMAGES

Fig. D1 — DFP on SO1465. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

Fig. D2 — MES on SO1465. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

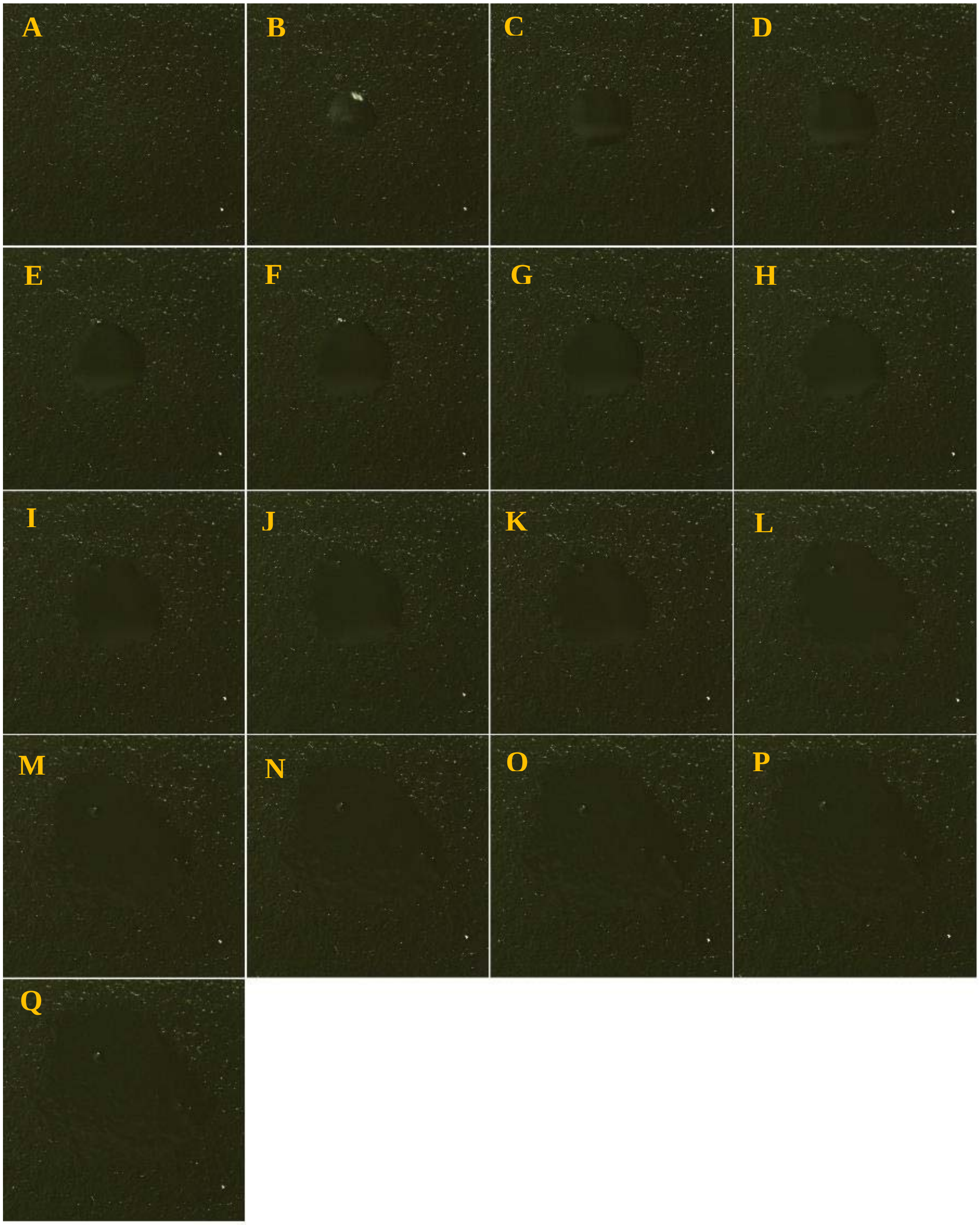
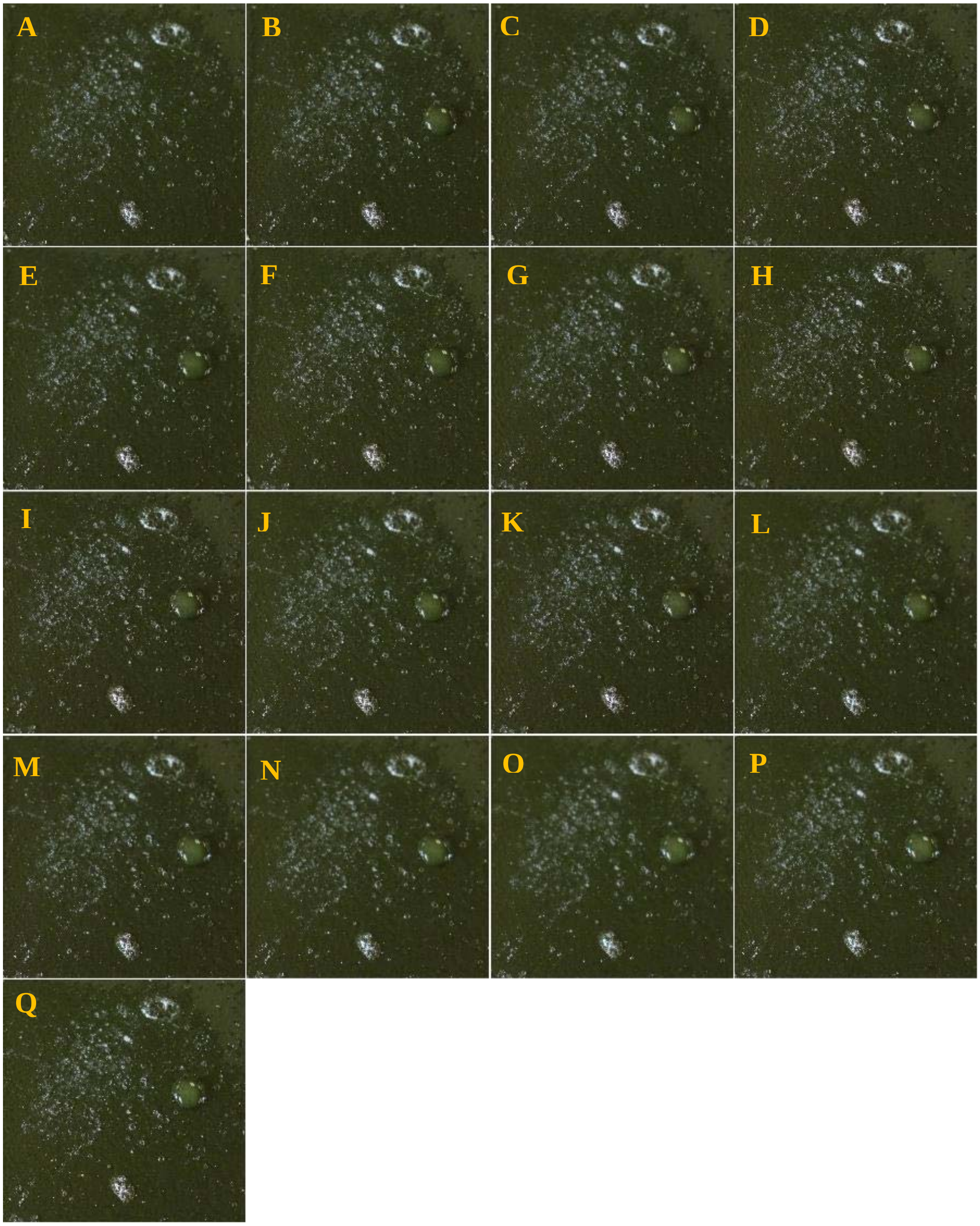


Fig. D3 — DMMP on SO1465. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix E

PAINTED COUPON IMAGES

Fig. E1 — DFP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 10 (L), 15 (M), 20 (N), 25 (O), and 30 (P) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

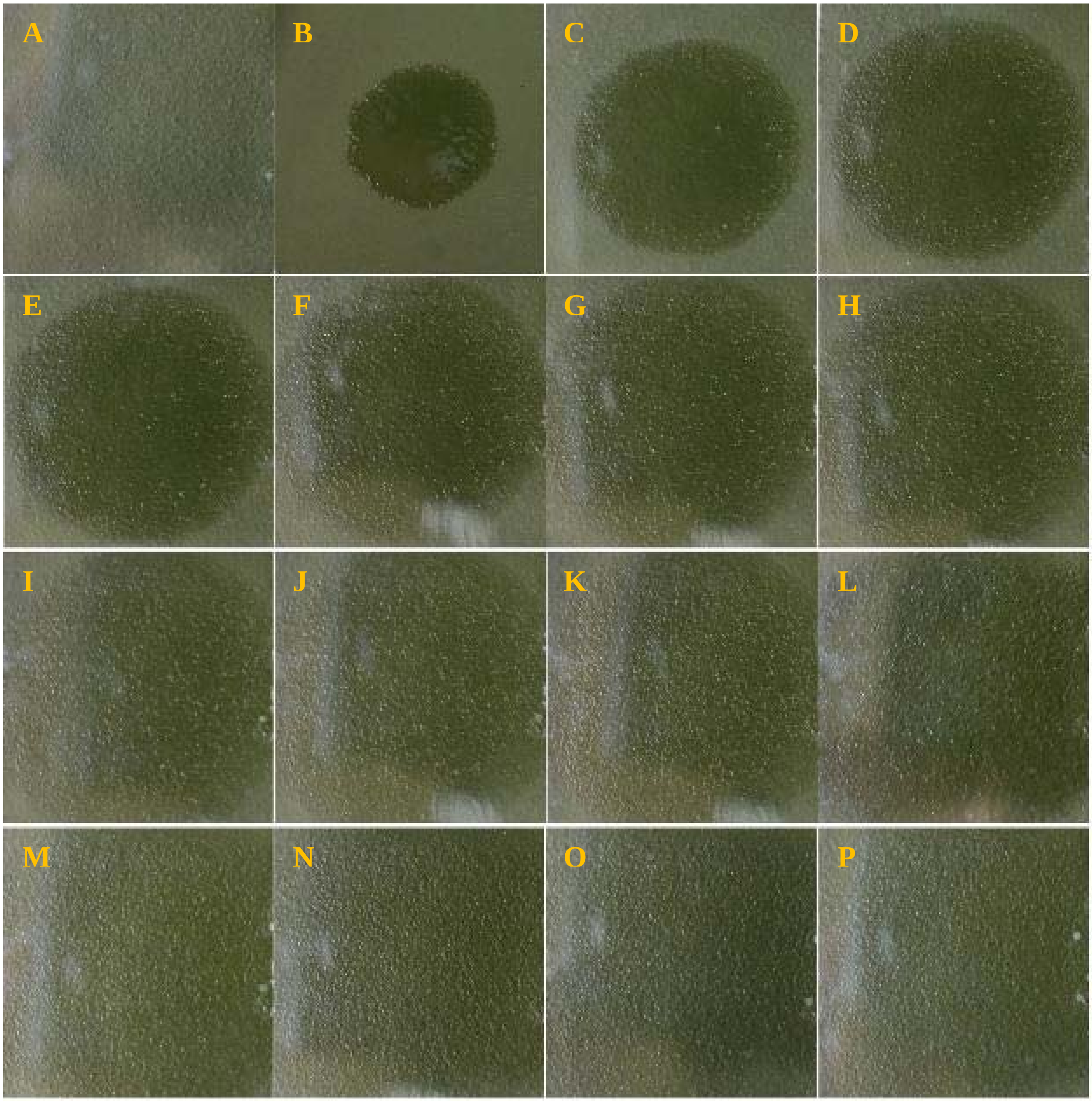


Fig. E2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

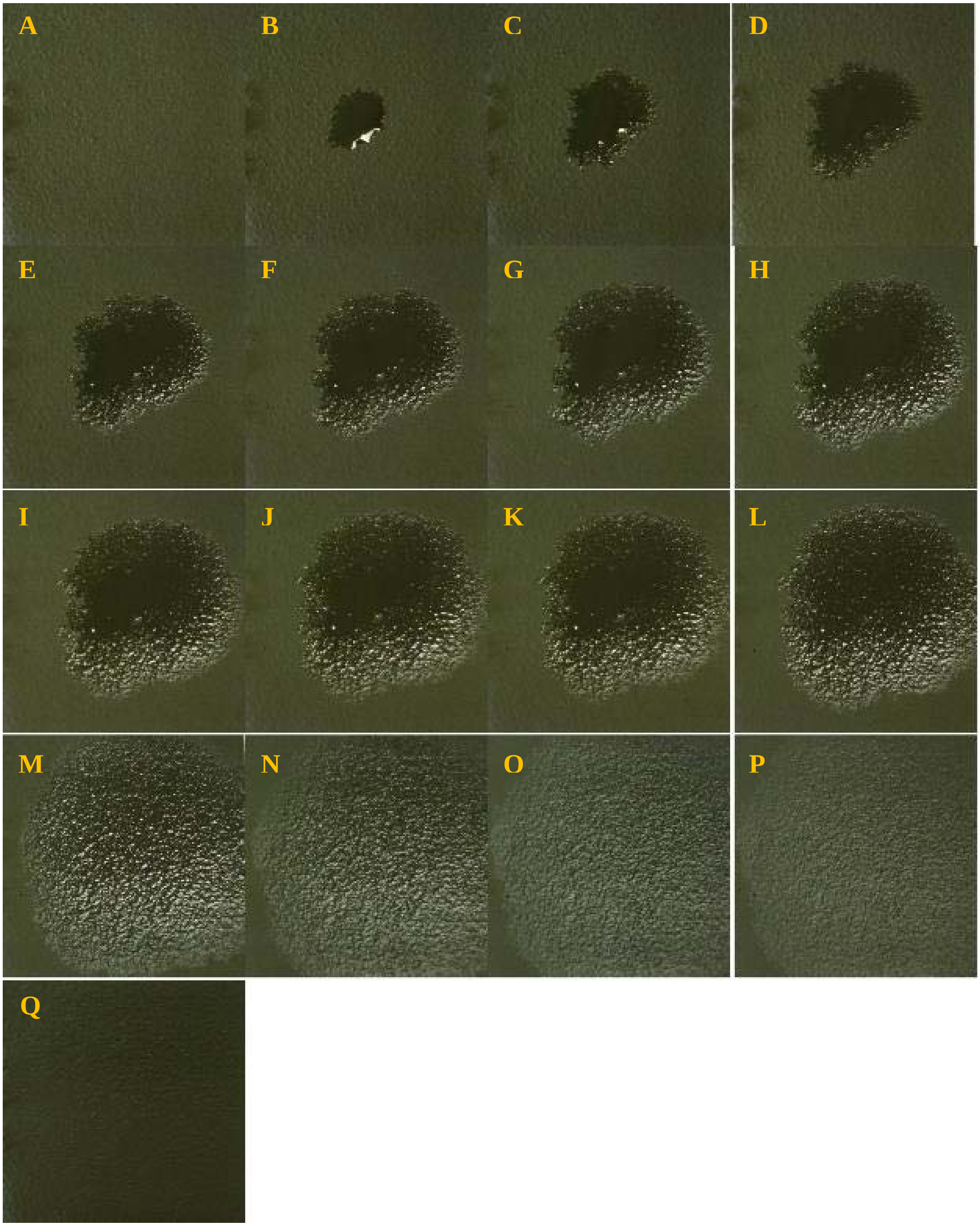
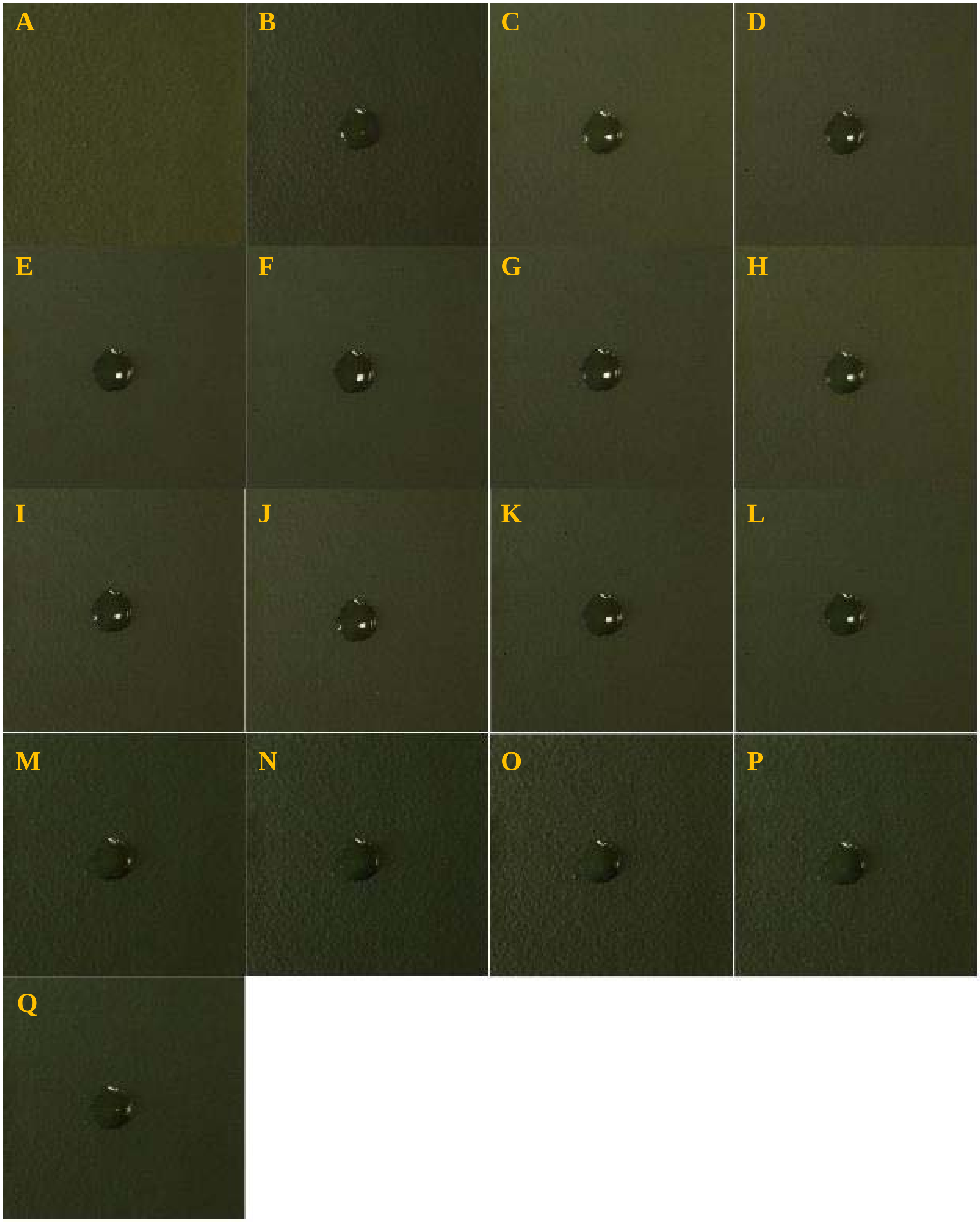


Fig. E3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix F

FOMBLIN Y LUBRICATED, PAINTED COUPON IMAGES

Fig. F1 — DFP on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

Fig. F2 — MES on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target.

Fig. F3 — DMMP on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min) min following application of the target.